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(54) PLASTISOLS

(71) We, RÖHM G.M.B.H., a German Body Corporate of Darmstadt, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to plastisols based on methyl methacrylate copolymers and organic softeners.

Plastisols are liquid to pasty mixtures which contain a particulate polymer in a liquid organic softener and, as a rule, inorganic fillers and which gel after heating to form solid compositions. Polyvinyl chloride is widely used as the particulate polymer, being particularly suitable for the preparation of plastisols in that it does not dissolve appreciably in the liquid softener at room temperature even after a lengthy storage time. Heating to at least 80 to 100°C results in dissolution of the polyvinyl chloride in the softener, the resulting solution having the properties of a solid owing to the high polymer concentration. After cooling to room temperature the gelled solution permanently retains its homogeneous quality.

However, polyvinyl chloride does have certain disadvantages as the polymer component of plastisols. Coverings prepared therefrom become yellowed, under the influence of light. Upon heating polyvinyl chloride may liberate hydrogen chloride which can lead to corrosion in production processes where heat is applied. Moreover, hydrogen can occur in dangerously high concentrations in the event of a fire or in the burning of waste. It has therefore been proposed in German Auslegesschrift 2,454,235 to prepare plastisols using methyl methacrylate polymers and organic softeners.

Although homopolymers and copolymers of methyl methacrylate do not have the above-mentioned disadvantages of polyvinyl chloride, they do not possess its special advantages in the gelling operation. Polymethyl methacrylate and any copolymers of methyl methacrylate form together with organic softeners durable plastisols which gel upon heating to e.g. 150°C. However, after the gelled material has been cooled to room temperature, the mixture proves in many cases to be unstable and exudes the softener again in liquid form. This is especially true with those softeners which are used on account of their low price, such as for example, phthalic acid esters. It is possible to increase the compatibility of methyl methacrylate copolymers with phthalate softeners by using acrylic or methacrylic acid esters of higher alcohols as comonomers. Although the softener-containing gelled masses which are prepared with these copolymers remain homogeneous at room temperature and below over a length of time, the plastisols prepared in this way gel even at room temperature within a few days. Plastisols stable during storage may, in general use, only be obtained with these copolymers if special softeners such as e.g. the relatively expensive dipropylene glycol dibenzoate or triethylhexyl mellitate are used. It is true that to a small extent the storability can also be improved by the use of relatively coarse polymer particles, but this gain in storability is offset by the disadvantage of there being a longer time required for the gelling operation and poorer film properties.

It is an object of the present invention to provide new and advantageous plastisols based on methyl methacrylate polymers.

According to the present invention we provide plastisols comprising an organic softener and an emulsion copolymer in the form of particles having a core/shell construction and consisting of:

(a) a core material compatible with the said softener and comprising a polymer derived from a monomer or monomer composition comprising:—

(A) 15 to 100% by weight of at least one monomer selected from alkyl acrylates containing at least 3 carbon atoms in the alkyl moiety, alkyl methacrylates containing at least 2 carbon atoms in the alkyl moiety, and styrene;

(B) 0 to 85% by weight of at least one monomer selected from methyl acrylate, methyl methacrylate and ethyl acrylate; and/or

(C) 0 to 20% by weight of one or more further radically polymerisable monomers; and

(b) a shell material which is incompatible with the said softener, the said shell material comprising a homopolymer of methyl methacrylate or a copolymer containing at least 80% by weight of units of methyl methacrylate and having a glass temperature of at least 50°C; the said core material (a) and the said shell material (b) being present in a weight ratio of 3:1 to 1:3, and the said emulsion copolymer and the said organic softener being present in a weight ratio of 10:3 to 1:10.

We have prepared plastisols in accordance with the present invention and have found that such plastisols are stable for a long period of time even when inexpensive softeners are employed. Such softeners are not exuded at room temperature after gelling.

The plastisols according to the invention may, if desired, further contain conventional fillers.

The core material in the emulsion copolymer particles preferably consists of a copolymer which is distinguished by good compatibility with softeners, particularly with phthalate softeners such as e.g. dioctyl phthalate. The core material alone would gel with the softeners even at room temperature within a short time. A homopolymer or copolymer of methyl methacrylate serves as the shell material, which is stable to softeners at room temperature, but which would not retain the softener in the homogeneous phase after gelling and cooling. In storage the shell material provides sufficient protection against premature gelling of the core material. If gelling has taken place at high temperature, the affinity of the softener for the core material is such that incompatibility with the shell material no longer leads to separation.

The compatibility of the core material with softeners is based on its content of alkyl acrylates or methacrylates containing respectively at least three or at least two carbon atoms in the alkyl moiety, and/or its content of styrene. Apart from a few exceptions such as, for example, polyethyl methacrylate, the affinity for the softener, especially a phthalic acid ester softener, of a homopolymer of these monomers is so high that the surrounding sheath of shell material would not offer any permanent protection against gelling at room temperature unless this affinity were attenuated by the presence of a more strongly polar monomer (B).

Stability in storage can be considered as sufficient for industrial application if the plastisol does not gel within 21 days at 30°C. A shorter storability of e.g. 3 to 5 days is sufficient in many cases, for example, when the plastisol is prepared and processed in the same factory. In comparison with plastisols consisting of polymers which are not made in shell form and which often gel within a few hours at room temperature and are therefore of limited industrial use, the plastisols according to the invention represent an important technical advance even with a storability of only a few days because the minimum storage time for industrial usage is still exceeded.

Since the affinity between the core material and softener depends closely on their chemical composition, the amount of polar monomer (B) is governed by the type of softener, by the type of monomer or monomer mixtures selected from groups (A) and (B) and, to a lesser extent, by the weight ratio of core material to shell material. The polymer composition is therefore always adapted to the softener to be used and allows only small variations from the optimum determined at any given time within the limits specified for components (A) and (B). In a preferred case, the core material contains as component (A) an alkyl methacrylate with 4 to 18 carbon atoms in the alkyl moiety and as component (B) methyl or ethyl acrylate or methyl methacrylate or mixtures thereof. Besides the monomers (A) and (B), further radically polymerisable monomers (C) can be employed in a proportion up to 20% by weight in the composition of the core material, particularly if their presence is desirable for special reasons. Such additional monomers include for example acrylic and methacrylic acid, their amides, nitriles, hydroxyalkyl esters and amino alkyl esters, vinyl esters of aliphatic carboxylic acids, vinyl pyrrolidone and vinyl imidazole.

Polymethyl methacrylate is particularly suitable as shell material. If a copolymer of methyl methacrylate is used instead, the proportion of comonomer or comonomers should be the smaller, the less polar they are. Monomers of the same type as group (A) are examples of non-polar monomers; their proportion in shell material preferably does not exceed 10%. More strongly polar monomers such as e.g. those of group (B) can form up to 20% by weight of the shell material. The choice of type and quantity of any comonomers optionally used in addition to methyl methacrylate is made such that the shell material, if it is homopolymerised, has a glass temperature of at least 50°C. Small proportions of strongly comonomers in the shell material, e.g. 0.5 to 8% of acrylic or methacrylic acid or acrylamide, have a favourable effect on the storage stability of the plastisols.

Since the plastisols are frequently used as coating agents, especially for metals, adhesion-assisting monomers are preferably employed in the preparation of the polymer. Examples of such monomers include polymerisable unsaturated carboxylic acids such as acrylic or methacrylic acid, and hydroxyalkyl esters or aminoalkyl esters of these acids. N-vinyl imidazole is especially effective. The adhesion-assisting effect of these comonomers is generally manifested at proportions of 0.1 to 5, preferably 1 to 2%. The adhesion-assisting comonomers can be polymerised into the core material and/or into the shell material.

The importance of the core/shell construction of the emulsion polymer is revealed by a comparison of plastisol prepared according to the invention with those mixtures in which the same softener is used with the same polymer quantity of the core material alone or of the shell material alone or with a mixture of these polymers. A copolymer was used for further comparison, whose overall composition coincided with the polymer composition of the plastisol according to the invention, although it was not prepared in a core-shell form.

TABLE I

Plastisol consisting of 2 parts of polymer and 3 parts of dioctyl phthalate, storage at 30°C, gelling 30 minutes at 150°C.

Polymer		Stability in storage (in days at 30°C)	Gelled product
Core material 30% BA, 70% MMA / Shell material PMMA	1:1	>21	Compatible
Copolymer 30% BA, 70% MMA		0	Compatible
PMMA		>21	Incompatible
Mixture PMMA + Copolymer 30% BA, 70% MMA (1:1)		0	Compatible
Copolymer 15% BA, 85% MMA		5	Incompatible

BA = n-butyl acrylate, MMA = methyl methacrylate, PMMA = Polymethyl methacrylate.

Determination of the optimal polymer composition for the dioctyl phthalate used as softener is illustrated in Table II.

TABLE

Example	Polymer		Stability in storage (in days at 30°C)	Gelled Product
	Core	Shell		
1	20% BA, 80% MMA	MMA	>21	Incompatible
2	30% BA, 70% MMA	MMA	>21	Compatible
3	35% BA, 65% MMA	MMA	12	Compatible
4	40% BA, 60% MMA	MMA	3	Compatible
Comparison Exp. 4a	Copolymer: 20% BA, 80% MMA		1	Incompatible
Comparison Exp. 4b	Mixture: 40% BA, 60% MMA +PMMA=1/1		Solidifies immediately	Compatible
5	45% BA, 55% MMA	MMA	1	Compatible
6	50% BA, 50% MMA	MMA	1/2	Compatible
7	35% BA, 65% MMA	95% MMA, 5% MAA	>21	Compatible
8	35% BA, 65% MMA	95% MMA, 5% MMAA	>21	Compatible
9	35% BA, 65% MMA	95% MMA, 5% AS	>21	Compatible
10	35% BA, 65% MMA	95% MMA, 5% MAS-	>21	Compatible
11	40% BA, 60% MMA	80% MMA, 20% MA	3	Compatible
12	15% nBMA, 85% MMA	MMA	>21	Incompatible
13	50% nBMA, 50% MMA	MMA	>21	Compatible
Comparison Exp. 13a	Copolymer: 25% nBMA, 75% MMA		>21	Compatible
Comparison Exp. 13b	Mixture: 50% nBMA, 50% MMA +MMA=1/1		Solidifies immediately	Compatible

TABLE (Continued)

Example	Polymer		Stability in storage (in days at 30°C)	Gelled Product
	Core	Shell		
14	70% nBMA, 30% MMA	MMA	6	Compatible
15	70% nBMA, 25% MMA, 5% MAS	MMA	>21	Compatible
16	70% nBMA, 30% MA	MMA	3	Compatible
17	20% nBma, 50% MMA, 30% St	MMA	>21	Compatible
18	10% EHA, 90% MMA	MMA	>21	Incompatible
19	20% EHA, 80% MMA	MMA	>21	Compatible
20	30% EHA, 70% MMA	MMA	19	Compatible
21	100% EMA	MMA	>21	Compatible
22	70% EMA, 30% MMA	MMA	>21	Compatible
23	80% i.BMA, 20% MMA	MMA	>21	Compatible
24	20% EHMA, 80% MMA	MMA	>21	Compatible
25	30% BA, 69% MMA, 1% VJ	99% MMA, 1% VJ	>21	Compatible

Explanation of the abbreviations:

MA	Methyl acrylate	i.BMA	Isobutyl methacrylate
MMA	Methyl methacrylate	EHMA	Ethylhexyl methacrylate
EMA	Ethyl methacrylate	EHA	Ethylhexyl acrylate
BA	n-butylacrylate	AS	Acrylic acid
nBMA	n-butylmethacrylate	MAS	Methacrylic acid
MAA	methacrylic acid amide	St	Styrene
MMAA	Methylol methacrylic acid amide	VJ	Vinyl imidazole

Whereas in Examples 1 to 25 the ratio by weight of core material to shell material is 1:1, in Examples 26 and 27 it is adjusted to 2:1 and 1:2 respectively.

Example 26

In a Witt pot (2 litres) with reflux cooler, agitator and feed vessel 0.1 g of ammonium peroxide persulphate and 3 g of C_{15}-paraffin sulphonate (trade name: emulsifier K30 Bayer AG) are dissolved at 80°C in 400 g of distilled water. Emulsion 1 is added to this solution with stirring over 2 hours at 80°C.

Emulsion 1 (core material):	417 g of MMA
	250 g of BA
	3.13 g of emulsifier
	0.20 g of initiator
	400 g of distilled water.

Emulsion 2 is subsequently added over 1 hour

Emulsion 2 (shell material):	333 g of MMA
	1.57 g of emulsifier
	0.10 g of initiator
	200 g of distilled water.

After everything has been added, the mixture is kept at 80°C for 2 hours and then cooled to approximately 25°C and spray-dried. The plastisol properties are tested as in Examples 1 to 25.

Stability in storage at 30°C: >21 days.

Gelled product: compatible.

Example 27

The procedure is as in Example 26 with the difference that the following emulsion is added over 1 hour:

Emulsion 1 (core material):	250 g of nBMA
	83 g of MMA
	1.57 g of emulsifier
	0.1 g of initiator
	200 g of distilled water.

Emulsion 2 is subsequently added over 2 hours.

Emulsion 2 (shell material):	666 g of MMA
	3.13 g of emulsifier
	0.2 g of initiator
	400 g of distilled water.

After everything is added the mixture is kept at 80°C for 2 hours and then cooled to 25°C and spray-dried. The plastisol properites are tested as in Examples 1 to 25.

Stability in storage at 30°C: >21 days

Gelled product: compatible.

The following Examples describe plastisols suitable for practical application (parts are parts by weight).

Example 28

An airless-spray plastisol is prepared from the following components,

20 parts of polymer powder according to Example 25

35 parts of dioctyl phthalate

50 parts of chalk

The homogenised mixture is sprayed onto an electrophoretically primed iron sheet in a thickness of 3 mm. The following gelling conditions are tested:

10 minutes at 180°C

15 minutes at 160°C

20 minutes at 140°C

25 minutes at 120°C

30 minutes at 100°C

Strongly adhering, flexible coverings are obtained in all cases.

Example 29

Airless-spray plastisols are composed as follows:

20 parts of polymer powder according to Examples 2, 13, 17, 23 and 24

35 parts of dioctyl phthalate

5 parts of trimethylolpropane trimethacrylate

0.2 parts of dicumyl peroxide

60 parts of chalk.

Degreased iron sheets approximately 3 mm thick are coated with the plastisols obtained and gelled for 10 minutes at 180°C. Flexible, strongly adhering coverings are obtained in all cases.

Example 30

Dipping plastisols are composed as follows:

20 parts of polymer powder according to Example 2, 13, 17, 23, 24, 25.

35 parts of dioctyl phthalate

5 parts of trimethylolpropane trimethacrylate

0.20 parts of cumol hydroperoxide

30 parts of chalk

10 parts of titanium dioxide.

Degreased iron sheets are coated by dipping and stoved for 10 minutes at 180°C. Strongly adhering, flexible coverings are obtained in all cases.

Example 31

A kneadable filler mass is prepared from:

20 parts of polymer powder according to Example 25

30 parts of dioctyl phthalate

60 parts of chalk

1 part of micronised porous silicic acid.

The kneadable mass is applied by hand to a thickness of approximately 5 mm on an electrophoretically primed sheet and stoved for 25 minutes at 120°C. A strongly adhering, flexible covering is obtained.

WHAT WE CLAIM IS:—

1. Plastisols comprising an organic softener and an emulsion copolymer in the form of particles having a core/shell construction and consisting of:—

(a) a core material compatible with the said softener and comprising a polymer derived from a monomer or monomer composition comprising:—

(A) 15 to 100% by weight of at least one monomer selected from alkyl acrylates containing at least 3 carbon atoms in the alkyl moiety, alkyl methacrylates containing at least 2 carbon atoms in the alkyl moiety, and styrene;

(B) 0 to 85% by weight of at least one monomer selected from methyl acrylate, methyl methacrylate and ethyl acrylate; and/or

(C) 0 to 20% by weight of one or more further radically polymerisable monomers; and

(b) a shell material which is incompatible with the said softener, the said shell material comprising a homopolymer of methyl methacrylate or a copolymer containing at least 80% by weight of units of methyl methacrylate and having a glass temperature of at least 50°C; the said core material (a) and the said shell material (b) being present in a weight ratio of 3:1 to 1:3, and the said emulsion copolymer and the said organic softener being present in a weight ratio of 10:3 to 1:10.

2. Plastisols as claimed in claim 1 wherein component (A) of the said monomer composition comprises an alkyl methacrylate containing 4 to 18 carbon atoms in the alkyl moiety.

3. Plastisols as claimed in claim 1 or claim 2 wherein component (C) of the said monomer composition comprises at least one monomer selected from acrylic and methacrylic acid; amides, nitriles, hydroxyalkyl esters and aminoalkyl esters of such acids; vinyl esters of aliphatic carboxylic acids; vinyl pyrrolidone; and vinyl imidazole.

4. Plastisols as claimed in any of the preceding claims wherein the said core material and/or the said shell material contain(s) units of at least one adhesion assisting monomer selected from polymerisable unsaturated carboxylic acids and hydroxyalkyl and aminoalkyl esters of such acids; and N-vinyl-imidazole.

5. Plastisols as claimed in any of the preceding claims wherein the said softener comprises an ester of phthalic acid.

6. Plastisols as claimed in claim 5 wherein the said softener comprises dioctyl phthalate or dibutyl phthalate.

7. Plastisols as claimed in any of claims 1 to 4 wherein the said softener comprises an ester of sebacic or azelaic acid or a polymeric softener.

8. Plastisols as claimed in any of the preceding claims containing at least one filler.

9. Plastisols as claimed in claim 8 wherein the said filler comprises chalk, kaolin or mica powder.

10. Plastisols as claimed in any of the preceding claims wherein the said emulsion copolymer and the said organic softener are present in a weight ratio of 2:3 to 1:2.

11. Plastisols as claimed in claim 1 substantially as herein described.

12. Plastisols as claimed in claim 1 substantially as herein described in any of the Examples.

13. A method of coating a substrate which comprises applying a coating of a plastisol as claimed in any of the preceding claims to a substrate and subsequently gelling the plastisol coating.

14. A method as claimed in claim 13 wherein the plastisol coating is applied in a thickness of 5 μm to 5 mm.

15. A method as claimed in claim 13 or claim 14 wherein the plastisol coating is gelled at 90 to 200°C.

16. A method as claimed in claim 13 substantially as herein described.

17. A method as claimed in claim 13 substantially as herein described in any of the Examples.

18. Coated substrates whenever prepared by a method as claimed in any of claims 13 to 17.

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